CHEMISTRY AND KINETICS OF CALCITE DISSOLUTION IN PASSIVE TREATMENT SYSTEMS[1]

by

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Abstract. Reaction of calcite with AMD is a key remediation process in anoxic limestone drains, SAPS, and many wetlands, but predictions of effluent quality are currently based mainly on rules of thumb and prior experience. The PHREEQC computer program (Parkhurst, 1995) can be used to calculate the progress of this and similar reactions, and aid in understanding, design and evaluation of these systems.

Simulations of the simple cubitainer tests of Watzlaf and Hedin (1993) showed good agreement with the cubitainer results and with the ALD effluent they represented. Simulations with varying pH and P_{CO2} in starting solutions show that alkalinities exceeding 50 mg/L in effluent can be produced only by influent AMD with pH less than 3.5 and/or P_{CO2} exceeding about 10^{-2} atm, and only by relatively close approach to equilibrium, suggesting that adequate retention times can be crucial.

Evaluation of observed influent and effluent waters in ALD's (Hedin and Watzlaf, 1994) shows that most are affected by inflows between the sampled inflow and outflow points and cannot be usefully simulated. The observed effluent at many ALD's producing high alkalinities requires oxidation and precipitation of Fe and/or Al within the drains, to generate additional H^+ that will cause added calcite dissolution. For a few well constrained ALD's, the calculated alkalinities are similar to the observed chemistry, though with significant scatter. At SAPS units, simulation can be used to evaluate the effects of sulfate reduction as well as calcite dissolution.

At pH values less than 5, calcite dissolution rates are strongly influenced by transport parameters such as flow velocity. Estimated calcite dissolution rates from ALD's and column experiments indicate little change in rate with pH, in contrast to published data for well stirred lab experiments. The dissolution rate is affected by concentration of SO_4, Fe, Al, Ca, P, and other trace solutes. The optimum contact time and sizing of ALD's will be dependent on these and possibly other parameters. Additional experiments are needed to evaluate these dependencies.

Additional key words: Anoxic limestone drains, successive alkalinity producing systems, acid mine drainage.

Introduction

Limestone, composed mainly of calcite, is an attractive material for neutralizing acid mine drainage because of its low cost relative to other commonly used alkaline materials such as NaOH or lime, and its ability to limit pH to values less than about 8.5. It is currently used extensively in passive treatment systems such as anaerobic wetlands, anoxic limestone drains (Hedin et al., 1994a, b), vertical flow systems such as SAPS (Kepler and McCleary, 1994, 1997), open limestone channels (Ziemkiewicz et al., 1994, 1997), and stream treatment with limestone sand (Zurbruch, 1996).

Many guidelines and techniques have been proposed for sizing and design of such treatment systems. For example, Watzlaf and Hedin (1993) suggest tests of limestone and AMD in "cubitainers" to estimate the alkalinity produced from the AMD at a proposed treatment site. Alternatively, values of 150 to 300 mg/L alkalinity added in a single stage of an ALD or SAPS are commonly taken as design guides (Hedin et al., 1994a), but field data indicate a wide range of

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variability. These and other guidelines and design criteria generally lack clear theoretical basis.

In this paper, the nature of calcite dissolution in AMD solutions is simulated with the PHREEQC computer program (Parkhurst, 1995). PHREEQC can perform aqueous speciation, reaction-path modeling, advective-transport modeling and inverse calculations. For the present paper, the speciation and reaction-path capabilities are used. For reaction path modeling, the program adds specified quantities of a mineral or solution to the initial solution (generally in the form of elemental quantities), and solves a set of simultaneous equations for mass balance of each element as well as charge and redox balance to obtain aqueous speciation. Undersaturated or supersaturated phases are added or removed until equilibrium or a specified degree of disequilibrium is attained. A series of such calculations can define the path of chemical change in the solution with increasing degrees of reaction.

Calcite Reaction with Acid Solutions

As an initial example of calcite dissolution, we consider a solution with a pH of 3.0 (as H_2SO_4) and P_{CO2} of $10^{-3.5}$ atm. at 25C. In a system closed to further exchange of CO2 with the atmosphere, we react 1 kg (approximately 1 liter) of this solution with successive small masses of calcite equal to about 10% of the amount required to reach saturation. With each small addition of calcite, the program recalculates the new equilibrium pH, P_{CO2}, HCO_3^-, Ca^{2+}, etc. The key equilibria involved are:

$$CO_2(g) + H_2O = H_2CO_3(aq) \qquad K_{CO2}=10^{-1.47} \text{ at } 25C \quad (1)$$

$$H_2CO_3(aq) = HCO_3^- + H+ \qquad K_1=10^{-6.4} \quad (2)$$

$$HCO_3^- = CO_3^{2-} + H^+ \qquad K_2=10^{-10.5} \quad (3)$$

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \qquad K_{CaCO3}=10^{-8.4} \quad (4)$$

Reactions (2) and (3) are essentially instantaneous, and reaction (4) represents the modeled calcite addition, so the equilibrium assumption is well justified for these reactions. Reaction (1) (exsolution of CO_2) is not possible in the saturated part of an ALD or SAPS, so the program models the natural reaction closely, unless other processes such as precipitation of Fe or Al hydroxide or gypsum are occurring. If the solution could interact with the atmosphere, the results would differ markedly.

The progress of reaction is shown in Figure 1. With increasing calcite dissolved, the pH increases

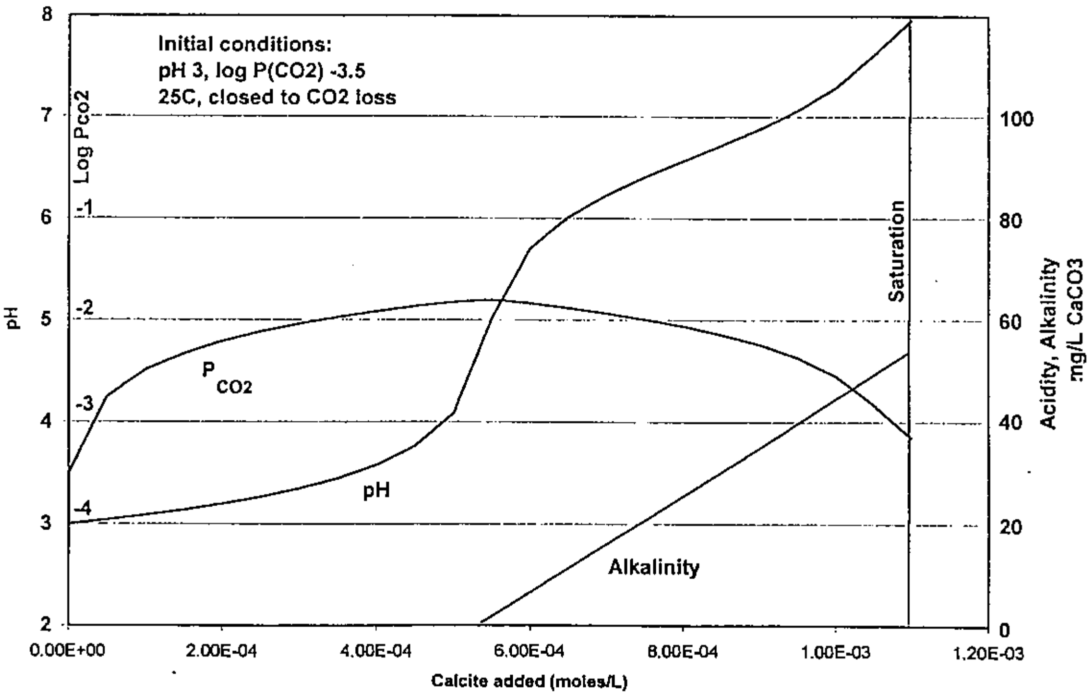


Figure 1. Calculated changes in pH, P_{CO2}, and alkalinity during addition of $CaCO_3$ to a solution with initial pH of 3 and P_{CO2} of $10^{-3.5}$ atm. at 25C, closed to CO_2 loss.

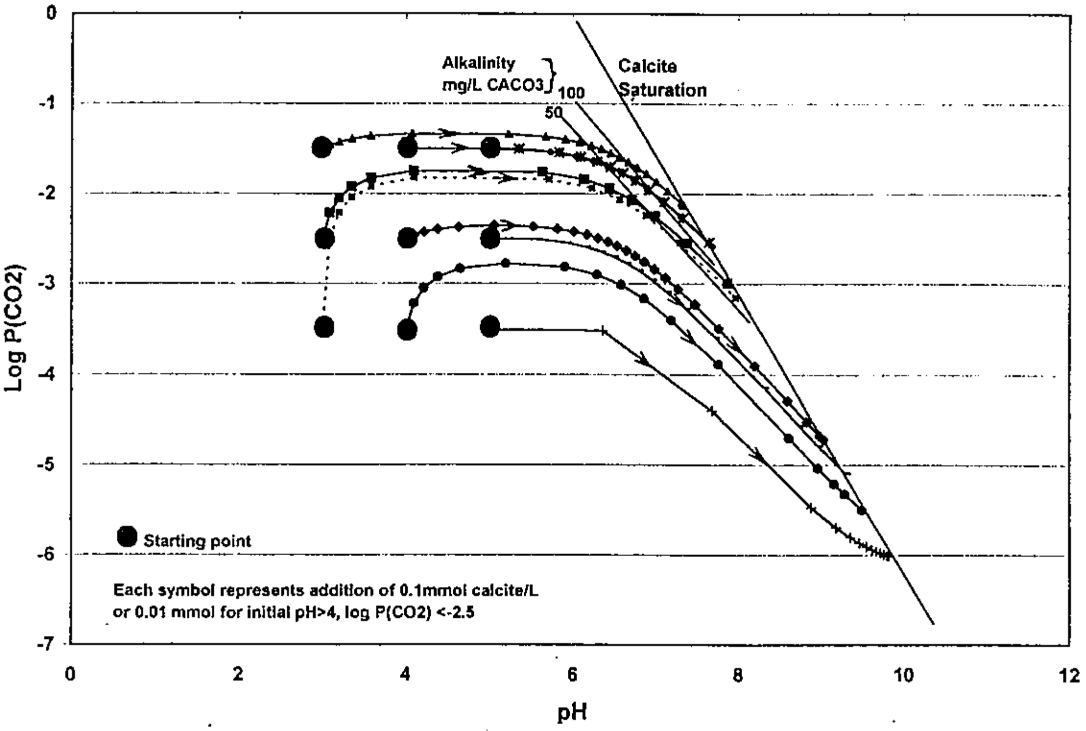


Figure 2. Calculated changes in P_{CO_2} as a function of pH during dissolution of $CaCO_3$ at 25C in a system closed to CO_2 loss, using PHREEQC. Starting solutions are shown with large dots. For initial pH 3 and/or $P_{CO_2}>10^{-2}$, each symbol represents the addition of 0.1 mmol $CaCO_3$; for higher initial pH and lower CO_2, symbols represent addition of 0.01 mmol $CaCO_3$. Contours at 50 and 100 mg/L $CaCO_3$ alkalinity show which solutions reach high levels of alkalinity along their reaction path.

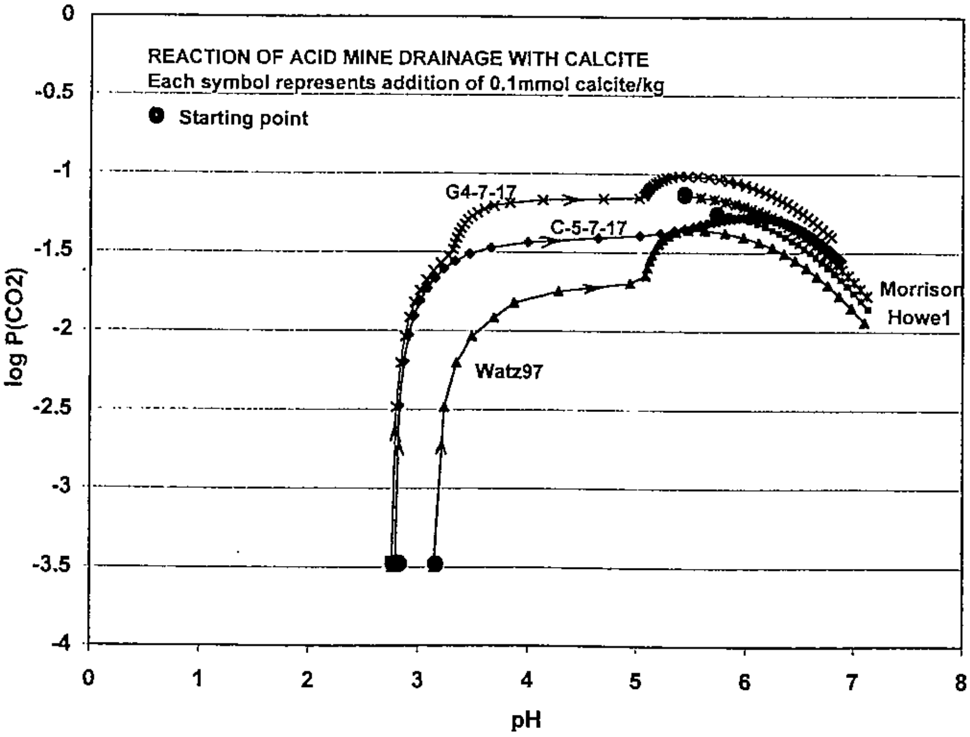


Figure 3. Calculated changes in P_{CO_2} as a function of pH for 5 AMD samples. Watz97 is column influent from Watzlaf (1997); Morrison and Howel are from Hedin et al. (1994b); G4-7-17 and C5-7-17 are inflow to SAPS systems at Cooney Pot Ridge Mine, Cambria Co., PA. Symbols as for Figure 2.

slowly at first, then more rapidly because of the logarithmic nature of pH, next more slowly because of HCO_3-H_2CO_3 buffering between pH 5.5 and 7, and then resumes more rapid increase to end at pH 7.95. The P_{CO2} increases rapidly from the initial value of $10^{-3.5}$ up to about 10^{-2}, where it levels off, initially because of the logarithmic representation, but after about 50% saturation it decreases because of conversion to HCO_3^-, to end at $10^{-3.1}$. Acidity (mainly as H^+ and H_2CO_3) decreases linearly to near zero, and alkalinity (mainly HCO_3^-) increases starting at pH 4.5, reaching a maximum of about 52 mg/L $CaCO_3$. Dissolved Ca increases linearly.

This example shows some of the complexity of calcite dissolution, specifically the non-linear variation in pH, and the increase and then decrease of P_{CO2}. Alkalinity and acidity are non-linearly related to pH, and other variables.

Reaction paths of P_{CO2} vs. pH for similar simulations of calcite reaction with acid solutions of varying initial chemistry are illustrated in Figure 2. For initial solutions with pH 5 and higher, the solution increases in pH and decreases in P_{CO2} with increasing reaction, and for starting P_{CO2} less than 10^{-2} atmospheres, finally equilibrates at negligible alkalinity (<20 mg/L $CaCO_3$). In contrast, the solution with initial P_{CO2} of $10^{-1.5}$ and pH 5 finishes with 138 mg/L alkalinity, indicating the key importance of starting P_{CO2}.

For solutions starting at more acid pH, the initial path is a marked increase in P_{CO2}, after which increased dissolution of calcite leads to increased pH.

For initial pH of 3, or initial P_{CO2} above about 10^{-2} atm., the final alkalinity is relatively high, from 50 to 300 mg/L $CaCO_3$. However, note that significant alkalinities are not attained until reaction is largely complete. For example, for starting conditions of pH 3, log P_{CO2} -3.5, if only half the saturation amount of calcite is dissolved (Saturation Index = -0.3), the alkalinity is only 6 mg/L rather than 52 as for complete equilibration. In most ALD's, calcite undersaturation is much larger (SI=-0.7 to -1.3, Watzlaf and Hedin, 1994).

Ideally, no Fe is precipitated in ALD's or SAPS during passage through the system (except for Fe sulfide precipitation in the organic layer of SAPS). The Fe enters the unit as Fe^{2+} or is reduced to this state on flowing through organic matter, and emerges from the unit as dissolved Fe^{2+}. The Fe^{2+} in the effluent from the ALD or SAPS is then oxidized and precipitated as ferric hydroxide in a following pond or wetland. The oxidation generates H^+:

$$Fe^{2+} + 0.25\,O_2 + 2.5\,H_2O = Fe(OH)_3 + 2\,H^+ \quad (5)$$

In order to precipitate appreciable $Fe(OH)_3$, the H^+ generated by precipitation must be neutralized by dissolved alkalinity acquired in the ALD or SAPS. Therefore, these units are not very effective for near-neutral waters unless appreciable alkalinities are reached in their effluent. The simulations make it apparent that a key characteristic of successful passive systems with appreciable acidity is a high degree of reaction with calcite in the ALD or SAPS, in order to attain high effluent alkalinity.

The above simulations are for simple acid solutions. The results are somewhat modified if additional solutes are present, though the general behavior is similar. Calcium has a significant effect, especially on the final pH, alkalinity and P_{CO2}. For example, the simple solution with pH 3, log P_{CO2} -3.5 equilibrates with calcite at pH 9.49, log P_{CO2} -5.49, alkalinity 13 mg/L. If 100 mg/L of Ca is present (as SO_4) in the starting solution, the final conditions are pH 8.54, log P_{CO2} -4.6, alkalinity 5 mg/L. In general, presence of Ca in the starting solution decreases the amount of calcite dissolved and the alkalinity reached.

Other constituents have complex effects. All increase the ionic strength, with small to moderate effects on activities. Increased SO_4 can lead to increased complexing of cations, including Ca. Presence of Fe^{2+}, Fe^{3+}, and Al are discussed below. Increases in Mg, Na and K can affect complexing of HCO_3 and other ligands.

The behavior for real AMD solutions is illustrated on Figure 3, which can be compared with Figure 2. The most striking effects are the upward kinks for some samples at about pH 5. These "kinks" result from precipitation of $Al(OH)_3$ and the resulting release of H^+ during this precipitation:

$$Al^{3+} + 3\,H_2O = Al(OH)_3 + 3\,H^+ \quad (6)$$

The H^+ causes the dissolution of additional calcite, tending to buffer the pH and increase P_{CO2}.

For sample G4-7-17, an additional kink is observed at about pH 3 because this sample contains Fe^{3+} which precipitates as $Fe(OH)_3$ or related compound, and has an effect similar to $Al(OH)_3$ precipitation. In ideal ALD's and SAPS, the influent should contain no Fe^{3+} or it is reduced by passage through a compost layer. However, effects of Fe^{3+} precipitation are apparently occurring in some ALD's and SAPS, as discussed below.

Prediction of Effectiveness of Limestone Reaction

The preceding simulations clearly show that the effectiveness of ALD's and SAPS depends in a complex way on the chemistry of the influent water. Watzlaf and Hedin (1993) proposed the "cubitainer test" as a means of predicting the effluent from a limestone treatment system. In this test, the water to be treated is placed in a collapsible plastic one-gallon container with limestone, and the generation of alkalinity is monitored for several days. Cubitainer tests closely approximated the effluent from several ALD's, and showed that in about 2 days the rate of alkalinity generation approached the value for much longer times.

In order to test whether the PHREEQE simulations could predict the effect of varying AMD chemistry, the two waters studied by Watzlaf and Hedin (1994) were reacted with limestone using PHREEQE. The results are shown graphically in Figure 4 (Howe Bridge and Morrison).

For the Howe Bridge site, alkalinity in the effluent, in the cubitainer test and in the equilibrium calculation are all in the range 200+/- 50 mg/L $CaCO_3$, and for Morrison they are all in the range 300+/-30. The relative values calculated for the two sites are in agreement with the field and lab results for the sites. The equilibrium calculation gives alkalinities that are 5 to 20% higher than the cubitainer and effluent for both sites, as might be expected if equilibrium was not reached in the cubitainer and field.

Comparison with Results for Anoxic Limestone Drain Effluents

Hedin et al. (1994b) present relatively complete data for two ALD's, Howe Bridge and Morrison, including water chemistry from several

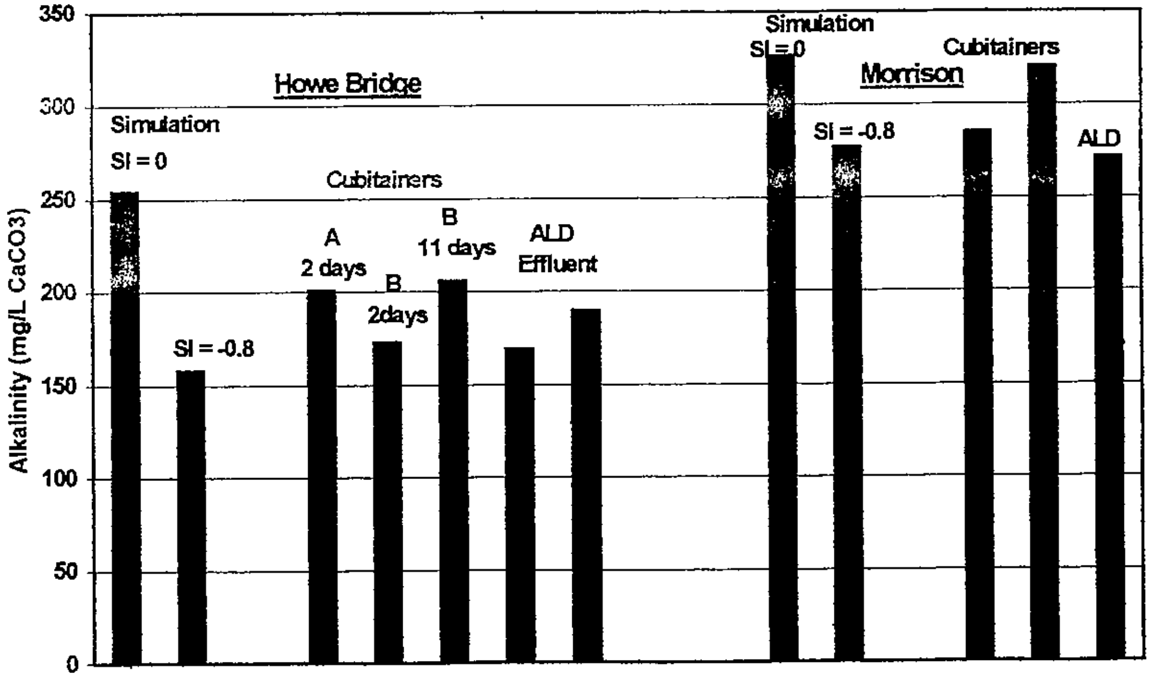


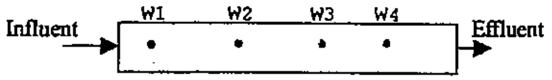
Figure 4. Comparison of alkalinities simulated with PHREEQC vs. cubitainer experiments and effluents of Howe Bridge and Morrison ALD's (Watzlaf and Hedin, 1993). Simulation results are shown for SI=0 (calcite saturation) and SI=-0.8 (16% of calcite saturation).

Table 1. Comparison of simulated compositions with observed compositions within ALD's.
Calcite added in simulations to equalize Ca to observed values.
Concentrations in mg/L, acidity/alkalinity in mg/L CaCO3. SI=Saturation Index

A. Howe Bridge

	Influent	Well 1	Well 1	Well 2	Well 2	Well 3	Well 3	Well 4	Well 4	Effluent	Effluent
		Obs.	Sim.	Obs.	Sim.	Obs.	Sim.	Obs.	Sim.	Obs.	Sim.
pH	5.6	5.9	6	6.1	6.4	6.3	6.6	6.3	6.6	6.2	6.5
Alkalinity	33	78	73	132	138	164	176	171	182	161	163
Acidity	482	448	500	404	435	360	397	353	391	373	410
Ca	159	175	175	201	201	216	216	218	218	211	211
SO4	1323	1314	1323	1339	1323	1340	1323	1339	1323	1329	1323
SI(calcite)	-2.65	-1.93	-1.83	-1.45	-1.1	-1.12	-0.77	-1.1	-0.72	-1.24	-0.88

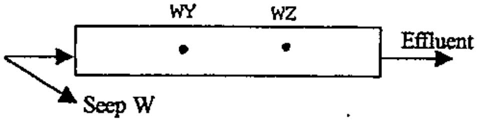
Other constituents that are essentially constant throughout: Al <1, Fe 279, Mn 41.



B. Morrison

	Seep W	Diluted	Well Y	Well Y	Well Z	Well Z	Effluent	Effluent
	Observed	13%	Obs.	Sim.	Obs.	Sim	Obs.	Sim.
pH	5.3	5.3	6.1	6.5	6.2	6.8	6.3	6.9
Alkalinity	23	19	201	200	269	267	267	271
Acidity	384	388	185	157	117	75	99	68
Al	1	1	0	0.8	0	0.4	0	0.2
Ca	119	101	187	187	221	221	230	230
Fe	216	185	188	157	169	149	151	147
SO4	1340	1137	1124	1137	1085	1137	1081	1137
SI(calcite)	-2.95	-3.01	-0.89	-0.75	-0.86	-0.26	-0.95	-0.16

Other constituents that are essentially constant throughout: K 6, Mn 42, Na 41.
Acidity is calculated from Fe, Al, Mn, H+



positions along the flow path in the ALD's. In Table 2 are listed the chemistry of the influent, four waters within the ALD, and the effluent from the Howe Bridge ALD. For each point, using PHREEQC, calcite was dissolved into the influent in amounts sufficient to produce the observed downflow Ca concentration. The resulting calculated alkalinity values are very similar to the observed values. The pH values in the calculation are close to the observed values, though they are consistently slightly higher. The calculated values for saturation index of calcite are also consistently lower than values for the observed waters because of the difference in pH.

Simulation of two internal waters and the effluent from the Morrison ALD shows similar agreement with observed alkalinity values. In this case, the field values for SO_4, Mn, and Mg indicate about 13% dilution of the inflow, which was simulated in the first step. In addition, the Fe decreases through the ALD, so this was simulated by adding small amounts of O_2 along with calcite, to approximately match the field values.

Extensive data on 21 ALD's is provided by Hedin and Watzlaf (1994). For example, effluents most commonly have calcite saturation indices of -0.7 to -1.0. A few samples are closer to saturation; the only two of these for which a contact time is available have very long contact time (700 and 1588 hrs).

Of the 21 ALD's, only 7 furnished data appropriate for comparison with simulations. The other 14 lack influent data for Ca, or show changes in SO_4 or Mn or increased Al indicating influx of additional water within the ALD. At 5 of the remaining 7 sites, Fe decreases significantly between the inflow and outflow, suggesting that it is being oxidized and precipitated. The increases and decreases in SO_4, Mn, Fe and Al indicate that a majority of these ALD's experience significant inflows of either more concentrated or more dilute AMD within the ALD, and that many have appreciable ingress of O_2, as pointed out by Hedin and Watzlaf (1994).

The 5 sites undergoing Fe loss have been modeled by adding sufficient O_2 along with calcite to achieve the observed effluent Fe value. The Morrison and Willi sites were diluted to equalize SO_4 and Mn with effluent values before reacting with calcite. Calcite was then added until the observed Ca in effluent was attained, or until saturation with calcite. The resulting calculated alkalinity is compared with the observed alkalinity of the 7 sites on Figure 5.

For 4 of the 7 sites, the calculated alkalinity is close to the observed alkalinity (Howe-1, Howe-2, Jennings, and Morrison). At REM-R, there is no increase in Ca, despite an increased pH and alkalinity, suggesting complications from unrecognized inflow. Rid-2R has somewhat less alkalinity than calculated, and Willi has far more. It seems likely that these ALD's are also subjected to unrecognized inflows.

Thus, the limited comparisons that can be made with this set of data indicate that most sites are complicated by unrecognized inflows, but that most of the sites with good control show reasonable agreement with the calculations.

Another set of simulations was made for two SAPS units for which data was available for the inflow and outflow chemistry (Cooney Pot Ridge G4 and C5). In this case the simulations showed that in order to approximately match the outflow composition, sulfate reduction in the organic layer was as important in alkalinity generation as reaction with limestone. The sulfate reduction was simulated by adding elemental carbon to the inflow water, along with calcite, and allowing pyrite to precipitate, to equalize with effluent Ca and Fe values. Using this procedure, the effluent acidity and the SO_4 concentration were closely approximated, but the calculated pH values were distinctly higher than the observed values.

Kinetics of Calcite Dissolution

The rate of calcite dissolution and/or the contact time of AMD with calcite are also important for effective neutralization of AMD. However, the calcite dissolution rate is dependent on a large number of variables. The following summarizes the kinds of effects that can be expected.

The rate of calcite dissolution in well stirred solutions has been extensively studied, as summarized by Plummer et al. (1978, 1979) and Chou et al. (1989). Plummer et at. (1978) show that for pH lower than about 5 in well stirred solutions, the calcite dissolution rate is proportional to concentration of H^+, and the rate is transport controlled (i.e., controlled by stirring rate, and diffusion of H^+ through the stagnant zone at the surface). The rate at pH 3 is therefore about 100 times the rate at pH 5. Above pH 5, the rate is dominated by surface reaction kinetics, and near saturation by the increasing rate of the back reaction causing precipitation. Chou et al. (1989) correct the equation of Plummer et al. (1978) for the back reaction effect.

If rates of dissolution in ALD's were as fast as the Plummer et al. (1978) equation, then AMD with pH

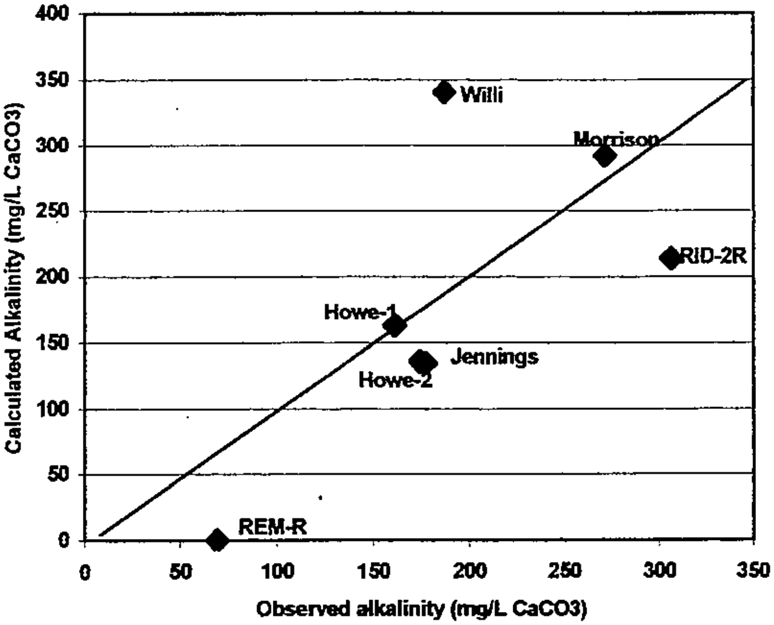


Figure 5. Comparison of calculated alkalinities with observed alkalinities of effluent of 7 ALD's (Hedin and Watzlaf, 1994). The line indicates equality of calculated and observed values. Calculated alkalinities are for Ca concentrations equal to the observed effluent.

Table 2. Rates of $CaCO_3$ dissolution in field and lab tests with AMD
Rates for Lab. Col. and Jennings are minimum rates.

	Units	Howe Bridge	Morrison	Lab Col.	Jennings
Inflow pH		5.6	5.3	3.14	3.3
Outflow pH		5.9	6.1	7.09	6.3
$CaCO_3$ dissolved[1]	mg/L	105	208[3]	315	322
Flow Rate	L/min	96	6.8	0.038	92
Contact time	hr	4.6	8.6	13.4	19
Ls size[2]	cm	3.2	7.6	1.3	14
Surface area	cm^2	$3.4x10^8$	$3.6x10^6$	$6.5x10^4$	$6.25x10^7$
Start/End points		Influent/Well2	SeepW/WellY	Inflow/Port2	Inflow/Outflow
Pore volume	L	$26.6x10^3$	$3.53x10^3$	3.1	$114x10^3$
Reference[4]		A	A	B	C
Rate[5]	$mmol/cm^2$-s	$1.7x10^{-8}$	$6.7x10^{-8}$	$3.6x10^{-9}$	$8.6x10^{-8}$

[1] Calculated from increase in Ca
[2] Based on personal communication from George Watzlaf (1999)
[3] Dilution of 13% allowed for
[4] References: A=Hedin et al. (1994b), B=Watzlaf (1997), C=Hedin and Watzlaf (1994)
[5] Rate=CP/AT, where C=$CaCO_3$ dissolved, P=Pore volume, A=Calcite surface area, T=Contact time for 1 pore volume.

2 to 4 would be neutralized very rapidly in ALD's and SAPS. However, the data of Hedin and Watzlaf (1994) show that effluent from some ALD's with acid inflows emerges still acid, despite theoretical contact times equivalent to some higher-pH sites that are successfully remediated. The writer has observed similar phenomena at SAPS receiving AMD with pH 2.5 to 3; after many days contact time the solution emerges with pH 3.2 to 3.5 and is many orders of magnitude undersaturated.

Table 2 summarizes some estimates of calcite dissolution rates from published data on field and lab experiments. Rates were estimated based on amount of Ca dissolved, contact time in the ALD or column, and an approximation of the calcite surface area. The surface areas are based on estimates of fragment size kindly provided by George Watzlaf. The rates are many orders of magnitude slower than for well-stirred solutions, and the rates for solutions with initial pH near 3 are very similar to solutions with initial pH of 5 to 6.

Further evaluation of the neutralization phenomenon shows several processes that may explain this behavior. First, the flow in ALD's and SAPS is very slow, rarely more than 10 cm/minute, so that the solution cannot be considered well stirred. Dissolution of calcite is no doubt limited by diffusion and slow mixing through a relatively thick zone adjacent to the calcite surface. Thus, the well stirred rates are not applicable to conditions in ALD's and SAPS.

Second, a coating of $CaSO_4$ has been observed to form on the surface of calcite dissolving in sulfate-rich solutions at pH values of 0.5 to 2.5 (Wentzler, 1971; Wentzler and Aplan, 1971). In order for Ca from calcite dissolution to diffuse away from the surface, the Ca concentration at the surface must be higher than the bulk solution. Many AMD's are near saturation with gypsum ($CaSO_4 \cdot 2H_2O$), and gypsum saturation may be exceeded at the calcite surface. Under well stirred conditions in the lab, this coating may be swept off, but under slow flow conditions it may significantly slow dissolution. AMD with relatively high SO_4 is presumably more susceptible to this phenomenon than low-SO_4 AMD. AMD with low pH may also promote formation of a gypsum coating, because of higher rates of calcite dissolution at the calcite surface.

Third, other dissolved species may affect calcite dissolution rate. For example, trace levels of PO_4, Cu and Sc are known to markedly slow calcite dissolution, apparently by adsorption to atomic-scale steps where dissolution is concentrated (Svensson and Dreybrodt, 1992). Gutjahr et al. (1996) observe decreases of dissolution rate of 50 to 90% in solutions with 10^{-7}M Fe, Cu and Zn (a few ug/L), and in Mg, Sr and Ba solutions of 10^{-4} molal (2 to 13 mg/L). Wentzler and Aplan (1972) found that for rapidly rotating disks in which surface coatings were swept off, calcite dissolution rate actually increased in Na_2SO_4 and $Fe_2(SO_4)_3$ solutions. Barton and Vatanatham (1976) found rates of dissolution were affected by Fe and Al, though most of the effect they observed appears to be due to buffering of pH by Fe and Al precipitation.

In view of these effects, it appears that the optimum design for ALD's and SAPS will depend on the chemistry of the specific AMD, its flow rate, the limestone size, temperature and other characteristics. Predictions regarding optimum design require additional experimentation and quantification on the effects of the chemical variables and on transport phenomena such as flow velocity.

Conclusions

1. The reaction path during dissolution of calcite in AMD solutions is complex. A computer simulation using PHREEQC can illustrate the influences of the many variables (influent pH, P_{CO2}, Ca, Fe, Al, temperature, etc.)
2. High effluent alklinities are achieved for samples with high influent P_{CO2} and/or low pH; for other AMD's the effluent alkalinity will be low to negligible.
3. Neutralization of AMD with low pH and appreciable Fe and Al requires dissolution of much more calcite than for simple acid solutions, and exhibits different types of buffering than simpler solutions. These differences must be taken into account in designing passive treatment systems.
4. Simulations using PHREEQC reasonably approximate the few available cubitainer tests, and may be a helpful substitute for such tests.
5. Many anoxic limestone drains show major effects of AMD inflows between the inflow and outflow points that have been sampled. As a result, modeling of the effluent is not possible. Oxidation and precipitation of Fe is also common, indicating O_2 influx, but can be modeled.
6. For the best constrained ALD's, PHREEQC simulations give a fair estimate of effluent alkalinity, but deviations are large enough that extraneous inflows are likely in at even these sites.
7. Calcite dissolution rate at pH values less than 5 is strongly affected by transport variables, and is not necessarily faster than at higher pH. Calcite dissolution rate is also affected by concentration of SO_4, Fe, Al, and certain trace constituents. Additional research is needed to utilize calcite dissolution rates in design of passive treatment systems.

Acknowledgements

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